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Controlled Ring-Opening Metathesis Polymerization by Molybdenum
and Tungsten Alkylidene Complexes

by

Richard R. Schrock, Steven A. Krouse, Konrad Knoll, Jerald Feldman,
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18. SUBJECT TERMS

Molybdenum

Tungsten

Alkylidene complexes

Bulky alkoxide ligands

Ring-opening metathesis polymerization (ROMP)

Cyclic olefins

Norbornene (NBE)

Endo,endo-5,6-dicarbomethoxynorbornene

Cyclopentene

Living polymers

Block copolymers

Low polydispersities

No secondary metathesis of polymer chains

Wittig-like reaction

Feast monomer

Retro Diels-Alder reaction

Low temperature column chromatography

Discrete, soluble polyenes

UV/vis spectra of polyenes

Solubilized polyacetylene

19. ABSTRACT

TUNGSTEN

A new, convenient preparation of $W(CH^tBu)(NAr)Cl_2^m(dme)$ ($Ar = 2,6$ -diisopropylphenyl) involves treatment of $W(NAr)(O^tBu)_2(CH_2^tBu)_2$ with PCl_5 in dimethoxyethane as a final step. From it a variety of complexes of the type $W(CH^tBu)(NAr)(OR)_2$ ($R = alkyl$ or fluoroalkyl) can be prepared straightforwardly in high yield. Analogous complexes of the type $Mo(CH^tBu)(NAr)(OR)_2$ also have been prepared. Complexes in which $OR = O^tBu$ will not react with ordinary olefins, but will react with strained cyclic olefins such as norbornene and cyclopentene to give living polymers from which the organic polymer can be cleaved by treatment with aldehydes. Polydispersities for norbornene polymers prepared in this manner are as low as 1.03. $Mo(CH^tBu)(NAr)(O^tBu)_2$ also will polymerize *endo,endo*-5,6-dicarbomethoxynorbornene (DCNBE) to give homopolymers and block copolymers (with NBE) with polydispersities in the range 1.10-1.15. A bis- CF_3 Feast monomer can be ring opened and the polymer cleaved with pivaldehyde to give (after pyrolysis) soluble polyenes, $^tBu(CH=CH)_{2x+1}^tBu$. Odd polyenes containing from 7 to 19 double bonds have been isolated by column chromatography employing five equivalents of monomer. Triblocks containing a 40-ene (average) central chain, capped by two polynorbornene chains (25 eq) have been prepared by related techniques. In this case the triblock with the expected molecular weight has been observed to form a high molecular weight material that is still soluble. The polymer with the expected molecular weight has been separated from the high molecular weight material by column chromatography.

CONTROLLED RING-OPENING METATHESIS POLYMERIZATION BY MOLYBDENUM AND TUNGSTEN ALKYLIDENE COMPLEXES

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Summary

A new, convenient preparation of $W(CH^tBu)(NAr)Cl_2(dme)$ ($Ar = 2,6$ -diisopropylphenyl) involves treatment of $W(NAr)(O^tBu)_2(CH_2^tBu)_2$ with PCl_5 in dimethoxyethane as a final step. From it a variety of complexes of the type $W(CH^tBu)(NAr)(OR)_2$ ($R = \text{alkyl or fluoroalkyl}$) can be prepared straightforwardly in high yield. Analogous complexes of the type $Mo(CH^tBu)(NAr)(OR)_2$ also have been prepared. Complexes in which $OR = O^tBu$ will not react with ordinary olefins, but will react with strained cyclic olefins such as norbornene and cyclopentene to give living polymers from which the organic polymer can be cleaved by treatment with aldehydes. Polydispersities for norbornene polymers prepared in this manner are as low as 1.03. $Mo(CH^tBu)(NAr)(O^tBu)_2$ also will polymerize *endo,endo*-5,6-dicarbomethoxynorbornene (DCNBE) to give homopolymers and block copolymers (with NBE) with polydispersities in the range 1.10-1.15. A bis- CF_3 Feast monomer can be ring opened and the polymer cleaved with pivaldehyde to give (after pyrolysis) soluble polyenes, $^tBu(CH=CH)_{2x+1}^tBu$. Odd polyenes containing from 7 to 19 double bonds have been isolated by column chromatography employing five equivalents of monomer. Triblocks containing a 40-ene (average) central chain, capped by two polynorbornene chains (25 eq) have been prepared by related techniques. In this case the triblock with the expected molecular weight has been observed to form a high molecular weight material that is still soluble. The polymer with the expected molecular weight has been separated from the high molecular weight material by column chromatography.

Introduction

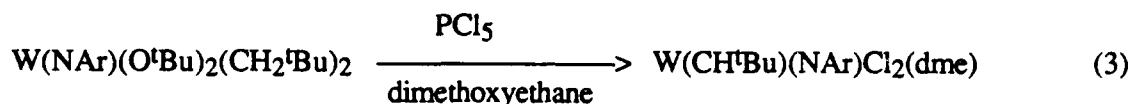
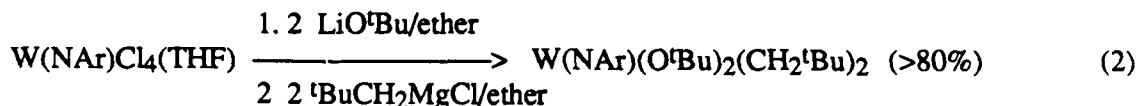
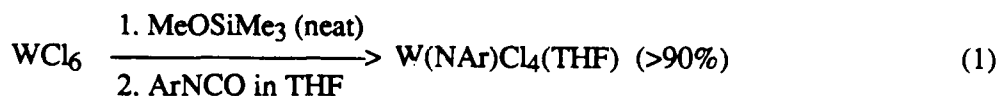
There are now several well-characterized catalysts that will ring open polymerize cyclic olefins, usually norbornene. The first one by Grubbs [1] is based upon a titanacyclobutane complex in which the rate-limiting step consists of opening of the TiC_3 ring. A tantallacyclobutane complex behaves in a related fashion [2]. Catalyst systems in which alkylidenes are the propagating species are of the type $\text{W}(\text{CHR})(\text{OCH}_2^t\text{Bu})_2\text{X}_2$ ($\text{X} = \text{e.g., halide}$) [3] and $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$) [4]. I will discuss some recent developments and applications of chemistry involving $\text{M}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ complexes ($\text{M} = \text{Mo or W}$).

Results and Discussion

The key to the chemistry of $\text{W}(\text{CHR})(\text{NAr})(\text{O}^t\text{Bu})_2$ complexes ($\text{R} = \text{alkyl}$), as far as ring-opening polymerization of cyclic olefins is concerned, is their virtual inactivity for metathesis of ordinary olefins. This result is striking since $\text{W}(\text{CHR})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ complexes will metathesize ordinary internal olefins at rates of at least 10^3 turnovers per minute [5]. We ascribe this difference to a dramatically lower electrophilicity of the tungsten in the *t*-butoxide derivatives. (We believe that the initial interaction between the metal and the olefin is essentially an acid/base interaction.) We do not believe the structure of a *t*-butoxide derivative differs dramatically from that of a hexafluoro-*t*-butoxide derivative (see below), and steric hindrance in a *t*-butoxide complex actually should be less than it is in the hexafluoro-*t*-butoxide analog. It should be noted that OR must be bulky enough to prevent oligomerization or polymerization of these electron deficient species through bridging alkoxide ligands.

We have discovered a new preparation of $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})\text{Cl}_2(\text{dme})$ that is relatively simple compared to the one we developed initially [5], and which can be scaled up easily. The two step sequence shown in equation 1 can be carried out without isolating $\text{W}(\text{O})\text{Cl}_4$, the product (virtually quantitatively) of the first reaction [6]. The second step is a well-known method of preparing imido complexes from oxo complexes [7]. The two steps shown in equation 2 proceed

in high yield. $W(NAr)(O^tBu)_2(CH_2^tBu)_2$ can be isolated as orange crystals from ether. The step shown in equation 3 is the key to this synthetic strategy. There is scant reference to PCl_5



as a means of replacing oxo ligands with chlorides [8a,b]. $AlCl_3$ is much more commonly used [8c-8e], a relatively recent example being the preparation of complexes of the type $W(CH^tBu)(OCH_2^tBu)_2X_2$ by treating oxo neopentyl complexes with aluminum trichloride [9]. We have noted that PCl_5 can be employed as a means of replacing both oxo *and t-butoxide* ligands by chlorides [10], but we have not yet found reference to reactions involving alkoxides in the literature. The mechanism is not known at this time. We suspect that it may proceed most readily with t-butoxide (relative to other alkoxides), since t-butoxide so readily loses the t-butyl carbonium ion. We have shown that similar reactions with other $W(NAr)(O^tBu)_2(alkyl)_2$ complexes in which the alkyl does not readily undergo α hydrogen abstraction yields $W(NAr)Cl_2(alkyl)_2$ complexes cleanly [11]. Therefore we postulate that the reaction in equation 3 proceeds via $W(NAr)Cl_2(CH_2^tBu)_2$ followed by α hydrogen abstraction and trapping of " $W(CH^tBu)(NAr)Cl_2$ " by dimethoxyethane.

An X-ray study of a prototypical catalyst, $W(CHPh)(NAr)[OCMe(CF_3)_2]_2$, showed it to be a pseudo-tetrahedral molecule in which the phenyl ring of the benzylidene ligand lay in the C_α -W-N plane (Figure 1) [12]. The phenyl ring of the benzylidene ligand points *toward* the imido nitrogen atom. This orientation of the phenyl ring, as well as orientations of all other ligands, can

be explained adequately solely on steric grounds. We propose that an olefin approaches an O/N/C face and adds to the W=C bond. The result is a trigonal bipyramidal tungstacyclobutane complex in which the ring occupies equatorial positions and the imido ligand an axial position (see, for example, the x-ray structure of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ [5]). The X-ray structure of $W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ [12] is closely related to that of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ except the WC_3 ring is planar in the $W(CH_2CH_2CH_2)$ complex and bent in the $W[CH(SiMe_3)CH(SiMe_3)CH_2]$ complex.

We now have been able to prepare $Mo(CH^tBu)(NAr)Cl_2(dme)$ [13] via routes that are entirely analogous to those used originally to prepare the tungsten analog [5]. So far we have not developed a route to the molybdenum catalysts that is as convenient as that we now use for the tungsten catalyst (equations 1-3). We find the same trends in metathesis activity for the Mo catalysts as for the W catalysts, namely that hexafluoro-*t*-butoxide catalysts are the most active for metathesis of ordinary internal olefins, and *t*-butoxide complexes virtually inactive. We also find that a given molybdenum catalyst is much less active than the tungsten analog, and molybdenacyclobutane complexes are much less stable than analogous tungstacyclobutane complexes toward loss of olefin. Another important difference between tungsten and molybdenum that correlates with their relative reactivities toward olefins is that tungsten appears to be much more reactive toward functionalities. Such differences will turn out to be extremely important in polymerization reactions of cyclic olefins that have a remote functionality on them. (We discuss an example below.)

We have shown that $W(CH^tBu)(NAr)(O^tBu)_2$ reacts smoothly with norbornene to give living polymers of the type $W[(CHC_5H_8CH)_xCH^tBu](NAr)(O^tBu)_2$ [4]. These complexes react rapidly with benzaldehyde to give $PhCH(CHC_5H_8CH)_xCH^tBu$ (~55% *trans*) and $W(O)(NAr)(O^tBu)_2$ in high yield. GPC analysis of the polymers thus obtained showed them to have the expected molecular weights and low polydispersities (as low as 1.03) consistent with a living catalyst system employing 50, 100, 200, and 400 eq of monomer. The reactions are fast at -40° . At 25° in C_6D_6 ~90% of the initiator is converted into the propagating alkylidene in the

presence of 10 eq of NBE, suggesting that propagation is slightly faster than initiation. This slight rate difference does not appear to adversely affect the polydispersities of the larger polymers whatsoever. The living polymers are very sensitive to moisture, and they decompose thermally in several days to yield as yet unknown products. No *cis/trans* isomerization occurs until samples have been kept for several days. Under such circumstances we cannot tell what the isomerization catalyst is. It could be some hydrolysis or thermal decomposition product instead of the living alkylidene itself.

$\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ also will ring-open polymerize NBE to give essentially monodisperse polymers containing up to 200 eq of monomer (Table 1) [14]. Although $\text{W}[(\text{CHC}_5\text{H}_8\text{CH})_x\text{CH}^t\text{Bu}](\text{NAr})(\text{O}^t\text{Bu})_2$ reacts readily with ethyl acetate, $\text{Mo}[(\text{CHC}_5\text{H}_8\text{CH})_x\text{CH}^t\text{Bu}](\text{NAr})(\text{O}^t\text{Bu})_2$ does not. Therefore norbornene can be polymerized in the presence of 10 eq of ethyl acetate. Entry 4 in Table 1 shows that polynorbornene prepared from 100 eq of NBE is virtually identical to that obtained in the absence of ethyl acetate, good evidence that the $\text{Mo}=\text{C}$ bonds are not destroyed to any significant extent by 10 eq of the ester during the polymerization reaction (10-15 min).

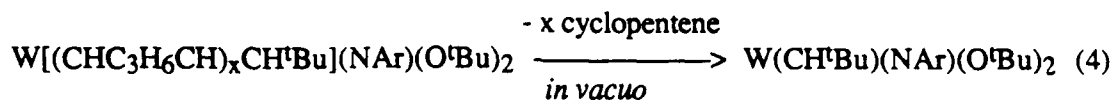
We also found that although *endo,endo*-5,6-dicarbomethoxynorbornene (DCNBE) could not be polymerized in a controlled manner by $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$, addition of DCNBE to $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ in C_6D_6 quantitatively converted it (vs. an internal standard) into a living polymer that has an alkylidene H_α signal at 11.64 ppm. 50 and 100 eq of DCNBE can be polymerized by $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ to give polymers with low polydispersity, characteristic of a living polymerization catalyst system (Table 1). The fact that the polydispersity of the polymer made with 100 eq of DCNBE (1.12) is not quite as good as that prepared from 100 eq of norbornene (1.06) suggests that the catalyst may be destroyed slowly, presumably by the ester carbonyl group in a Wittig-like reaction. This is supported by the fact that the polymer prepared using 200 eq of DCNBE, although it has the expected molecular weight relative to the polymer prepared employing 100 eq of DCNBE, has an even higher polydispersity (1.22).

If a living polymer containing 20 eq of NBE is prepared and 20 eq of DCNBE is added to

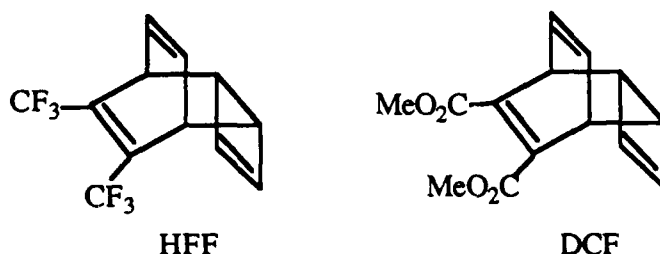
it, an ^1H NMR spectrum shows that the H_α resonance characteristic of a living norbornene polymer is completely replaced by that characteristic of a living DCNBE polymer, and that the remainder of the spectrum is a virtual composite of that for the two homopolymers [14].

The results of two critical experiments are shown as the last two entries in Table 1. Living block copolymers were prepared via the sequential addition of 50 equivalents of DCNBE and 200 eq of NBE (and *vice versa*) to $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ over a period of ~ 15 min. The polymer was cleaved off with benzaldehyde and characterized in the standard manner [14]. The number average molecular weights and the polydispersities of the two block copolymers are virtually identical. The slightly higher M_n and polydispersity in the 50/200 copolymer could be ascribed to some destruction of alkylidene catalyst centers during polymerization since chain propagating species are exposed to ester for a longer period. However, it is clear that no significant amount of catalyst is destroyed in either experiment, and we must conclude on the basis of these and the results described above that at least 100 eq of ester functionality (in 50 eq of monomer) is tolerated absolutely on the time scale of a typical experiment (15 minutes). To our knowledge this is the first report of a controlled polymerization of a norbornene that is derivatized with an ester functionality, and the first report of polymerization of DCNBE. (Polymerization of the *endo,exo* derivative by a classical system has been reported [15].)

We have briefly explored ring-opening polymerizations of other olefins. For example, 50 eq of cyclopentene are polymerized at 25° by 0.04 M $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ in benzene to give a living cyclopentenamer. At $+60^\circ$ the mixture contains $\sim 95\%$ monomer, while at -60° the mixture contains $\sim 95\%$ polymer. When cyclopentene is removed *in vacuo*, $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ is recovered in high yield (equation 4). All these characteristics are typical of classical cyclopentene polymerization systems [16], although to our knowledge this is the first time that a completely reversible, *living* system has been observed. Loss of cyclopentene can be prevented by adding several equivalents of NBE as a capping agent. We have prepared cyclopentene/NBE block copolymers, but so far have not investigated them in detail.



We thought it likely that we could polymerize "Feast monomers" [17] in a controlled fashion. This has proven to be possible for both HFF (employing either $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ or $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$) and DCF (employing $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$). Polymerization



of DCF with $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ could prove to be important (if a good route to the molybdenum catalyst can be developed) since dimethylacetylenedicarboxylate is so much cheaper and more readily available than hexafluoro-2-butyne. Five equivalents of HFF were added to $\text{W}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$ in toluene at 25°. The polymer was cleaved off with pivaldehyde and the retro Diels-Alder step carried out at 160° for 4 minutes (Scheme 1). Crude, pentane soluble $^t\text{Bu}(\text{CH}=\text{CH})_{2x+1}^t\text{Bu}$ was isolated in ~90% yield and the individual oligomers isolated by low temperature column chromatography on silica gel under argon [18]. The 13-ene and 15-ene are somewhat air-sensitive while the 17-ene and 19-ene are very air sensitive. Films that are crystalline by eye and macroscopic crystals have been observed in several cases. The ^1H NMR spectrum of the 11-ene is shown in Figure 2. We assign the signal at ~5.8 ppm to the olefinic protons on the same carbon atom as a *t*-butyl group. The fact that this resonance consists of primarily one doublet is evidence that the configuration about the terminal double bond, and probably also at least the next double bond is either *cis* or *trans* (we presume *trans*). Evidence that the all *trans* isomer is not necessarily preferred for the shorter polyenes, and/or that *cis/trans* isomerization is not as rapid in shorter polyenes consists of the fact that the 7-ene shows a complex pattern at 5.8 ppm, i.e., a mixture of isomers is present. After the 7-ene has been heated to 200°

for seven minutes in toluene in an autoclave, the pattern at 5.8 ppm simplifies considerably.

In Figure 3 are shown the UV/VIS spectra of the 7-ene, 9-ene, 11-ene, 13-ene, and 15-ene. The three band pattern corresponds to that expected for a polyene [19]; the somewhat solvent dependent maxima for the three strongest absorptions are listed in Table 2. The maxima shift and sharpen after heating to 200° in toluene for seven minutes, we presume because of *cis* to *trans* isomerization. Unfortunately at this point we do not know that solely the all *trans* isomer is produced under these conditions.

The EI mass spectra of the 7-ene, 9-ene, 11-ene and 13-ene are as expected, the parent ion being the strongest and the doubly charged parent becoming obvious for the longer polyenes.

In other preliminary studies we have prepared and investigated several triblocks containing polyacetylene in the middle, and polynorbornene at the ends. One was prepared in toluene employing $\text{Mo}(\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$, 25 eq of NBE, 20 eq of HFF, 25 eq of NBE, and benzaldehyde as the cleaving/capping reagent. If the triblock is heated in solution at 125° for 15 minutes, the resulting *entirely soluble*, red polymer consists of (by GPC studies in dichloromethane) a fraction with the expected molecular weight and low polydispersity, and a much higher molecular weight fraction (~100x) with a relatively high polydispersity (Figure 3a). If the retro Diels-Alder reaction is carried out in a film, the now only ~10x molecular weight fraction has an extraordinarily low polydispersity (Figure 3b). The low molecular weight fraction can be separated by column chromatography and shown to have a UV/VIS spectrum with a maximum absorption at 482 nm, corresponding to relatively short (20-ene) conjugated chains, instead of the expected 40-ene chains; it appears to form the high polydispersity, high molecular weight material slowly in solution. We are reluctant to draw conclusions based on v_{max} values since we know that considerable decomposition of the triblock mixture occurs upon chromatography, even at -25°; the low molecular weight material what is isolated therefore may not be representative of what was initially present. At this time we do not know whether the high MW material results from cross-linking, or is simply an insoluble crystalline form. We favor the former and hope to distinguish between them soon.

These results (and those recently obtained by Grubbs) provide the first glimpse of some of

the things that are now possible in the area of ring opening metathesis polymerization with well-characterized catalysts whose activity can be closely controlled and predicted. Soon we expect to be able to prepare catalysts even more simply and to begin elaborating, clarifying, and applying this technology to areas where well-defined oligomeric or polymeric materials are desirable.

Acknowledgments

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Table 1

Polymers prepared from norbornene and *endo,endo*-5,6-dicarbomethoxynorbornene.^a

| Eq monomer | M_n (theory) | M_n (found) | Polydispersity |
|-----------------------|----------------|---------------|-------------------|
| 50 NBE | 4870 | 13500 | 1.11 |
| 100 NBE | 9580 | 22100 | 1.06 |
| 200 NBE | 19000 | 48600 | 1.04 |
| 100 NBE | 9580 | 21900 | 1.07 ^b |
| 50 DCNBE | 10700 | 17400 | 1.11 |
| 100 DCNBE | 21200 | 37700 | 1.12 |
| 200 DCNBE | 42200 | 63300 | 1.22 |
| 50 + 200 ^c | 29500 | 59900 | 1.09 |
| 200 + 50 ^d | 29500 | 57200 | 1.06 |

^a All reactions were performed in the same manner [14]. Molecular weights are relative to polystyrene; approximate true molecular weights can be obtained by dividing by 2.2.

^b Reaction performed in the presence of 10 eq of ethyl acetate.

^c 50 eq of *endo,endo*-5,6-dicarbomethoxynorbornene followed by 200 eq of norbornene.

^d 200 eq of norbornene followed by 50 eq of *endo,endo*-5,6-dicarbomethoxynorbornene.

Table 2

UV/VIS maxima (three lowest energy peaks in nm) for t-butyl capped polyenes (resolution 2 nm).

| <u>ene</u> | <u>pentane</u> | | | <u>dichloromethane</u> | | |
|-----------------|----------------|-----|-----|------------------------|-----|-----|
| 5 | 344 | 326 | 312 | 350 | 334 | 318 |
| 7 | 392 | 370 | 352 | | | |
| 7 ^a | 394 | 372 | 354 | 404 | 380 | 362 |
| 9 | 428 | 404 | 382 | | | |
| 9 ^a | 432 | 406 | 384 | 444 | 418 | 396 |
| 11 | 456 | 428 | 406 | | | |
| 11 ^a | 466 | 438 | 414 | 480 | 450 | 428 |
| 13 | 478 | 448 | 422 | | | |
| 13 ^a | 490 | 460 | 434 | 508 | 476 | 452 |
| 15 | 492 | 464 | 438 | | | |
| 15 ^a | 508 | 478 | 454 | 528 | 496 | 472 |

^a Isolated samples were heated to 200° for an additional 7 min in toluene.

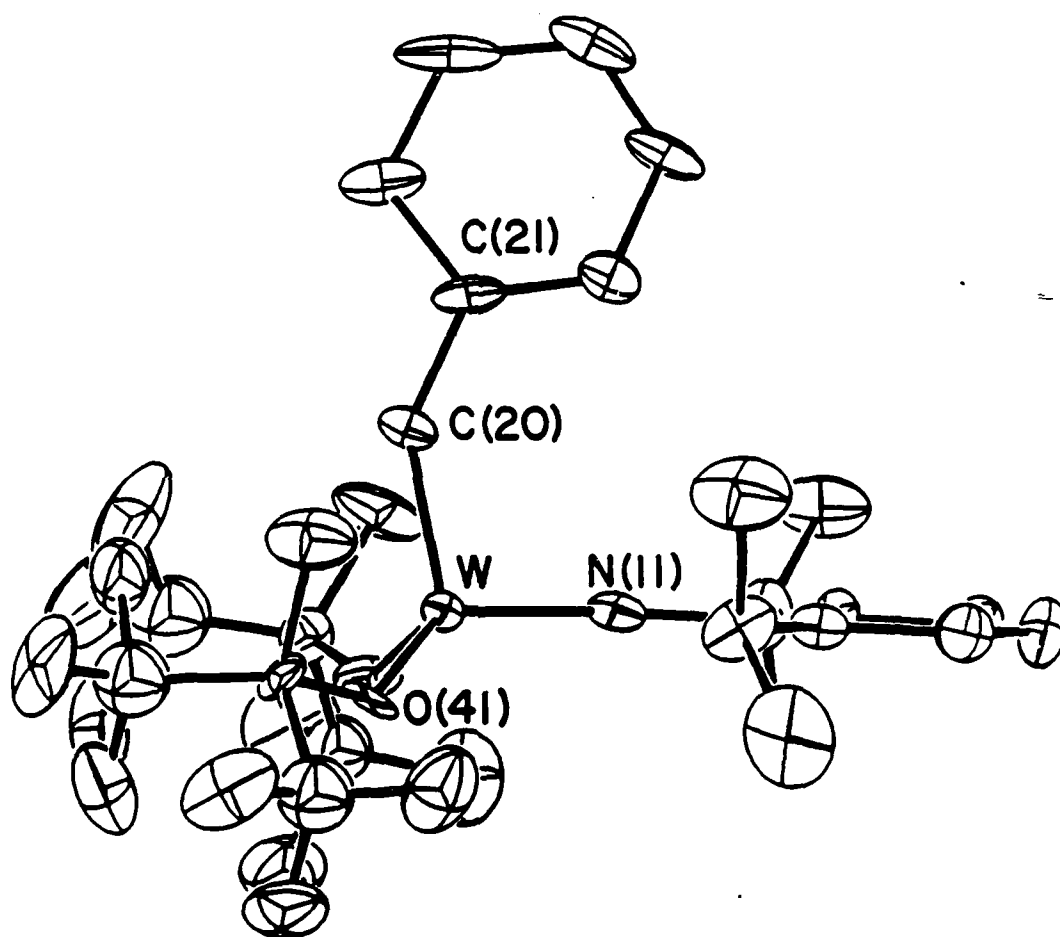
Fig. 1. A view of $W(CHPh)(NAr)[OCMe(CF_3)_2]_2$ looking down onto the C(20)-W-N(11) plane.

Fig. 2. The olefinic region of the 1H NMR spectrum of the 11-ene in C_6D_6 .

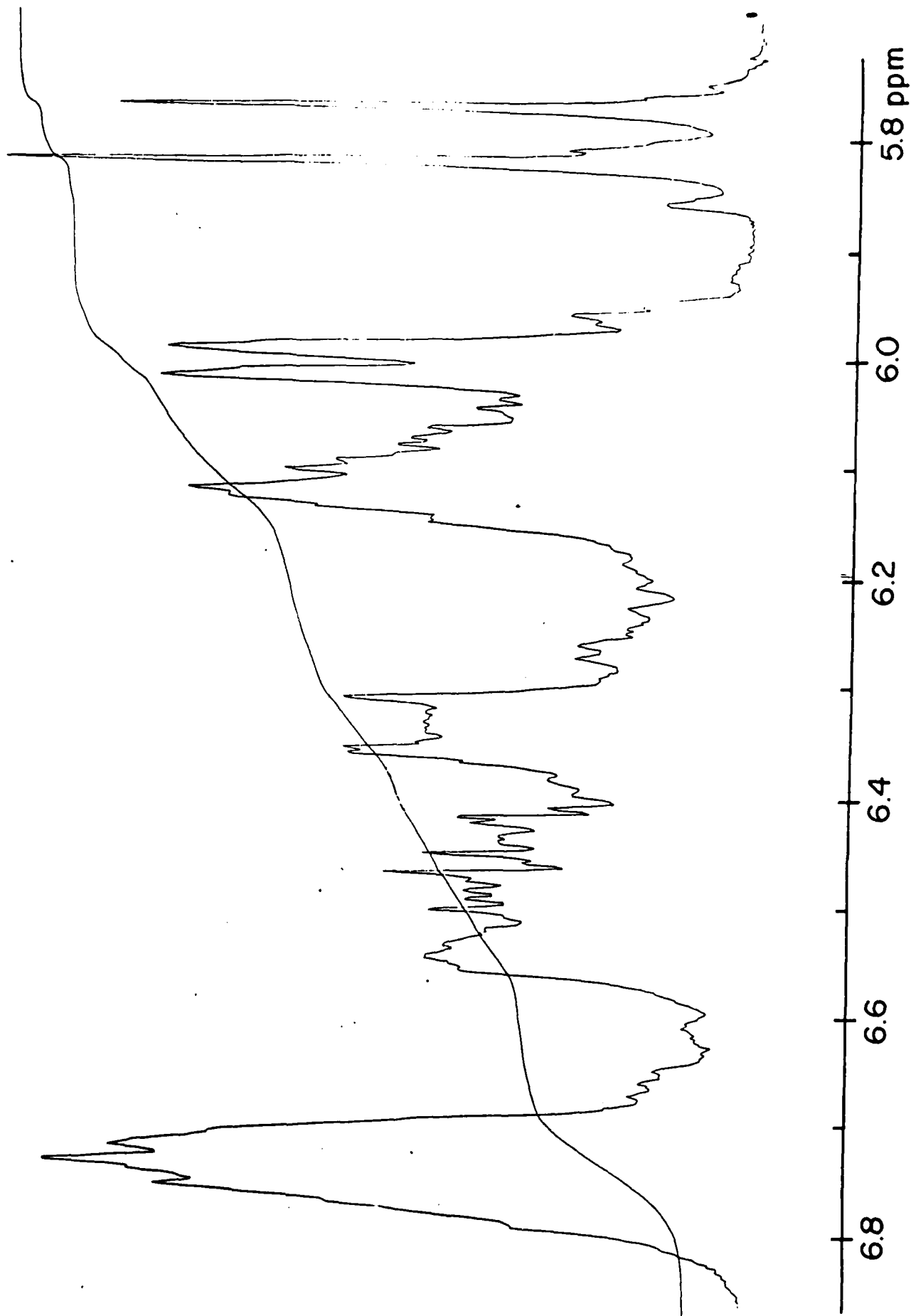
Fig. 3. UV/VIS spectra of t-butyl-capped polyenes prepared as shown in the Scheme, isolated by low temperature chromatography on silica gel, and heated to 200° for an additional 7 min in toluene in order to isomerize the majority of *cis* bonds to *trans*.

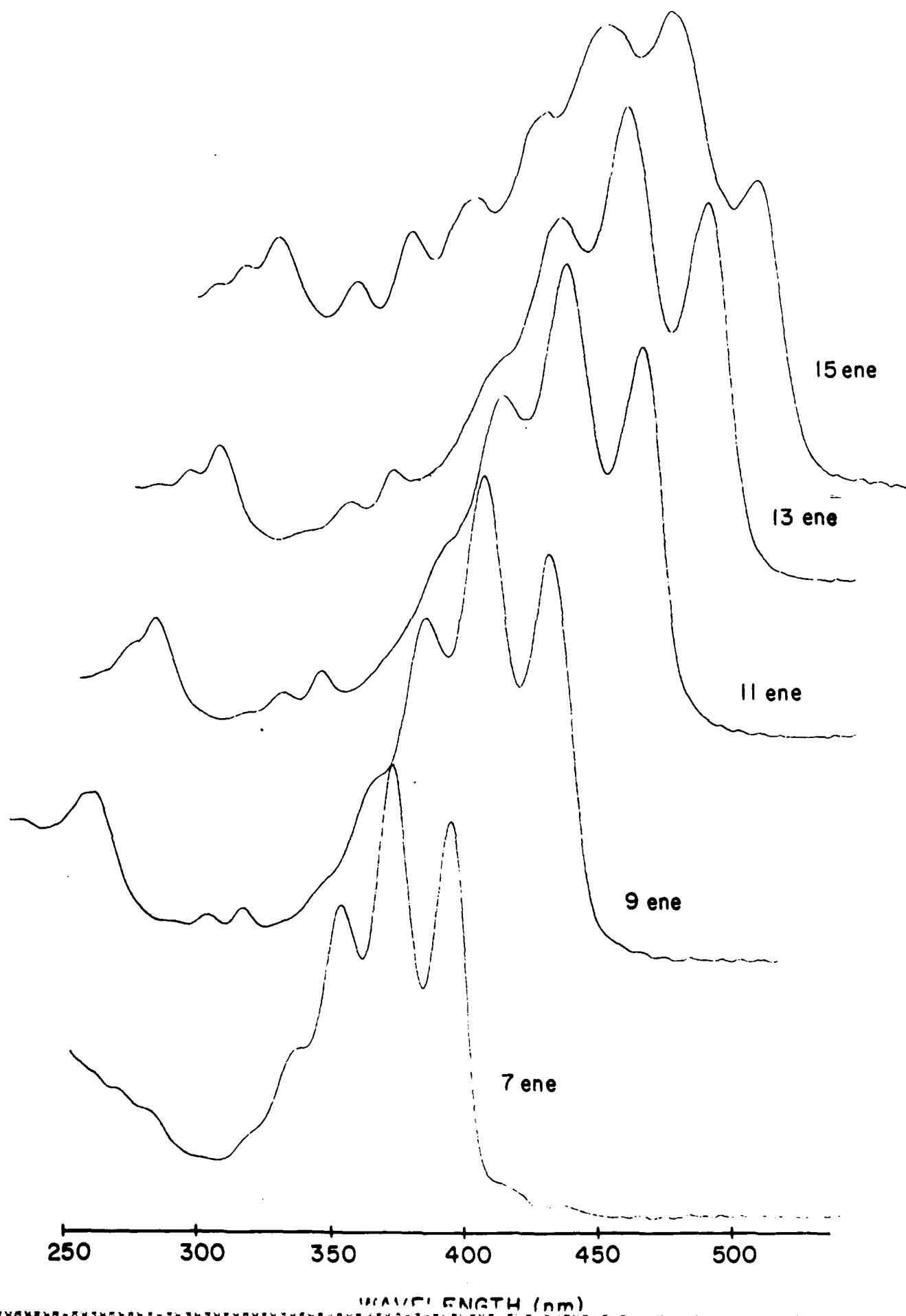
Fig. 4 GPC studies in dichloromethane of the 25NBE/polyene/25NBE triblock prepared using $Mo(CH^tBu)(NAr)(O^tBu)_2$ as the catalyst, 20 eq of HFF, and benzaldehyde as the capping reagent (benzylidene cap): (a) precursor polymer heated for 5 hrs in toluene at 50° ; (b) precursor polymer heated for 15 min at 90° as a thin film.

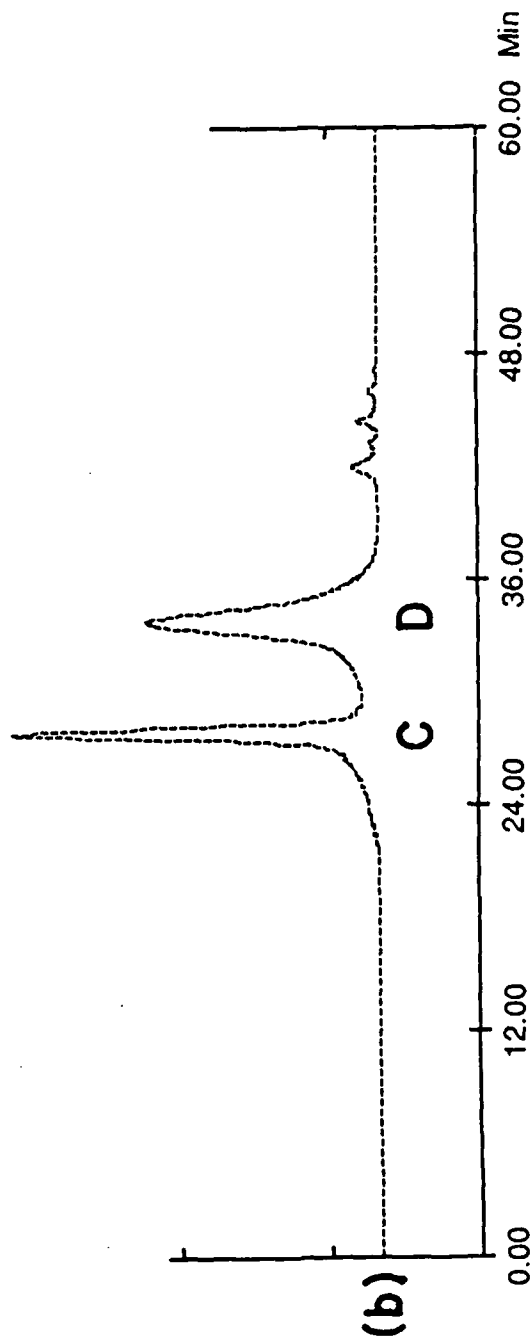
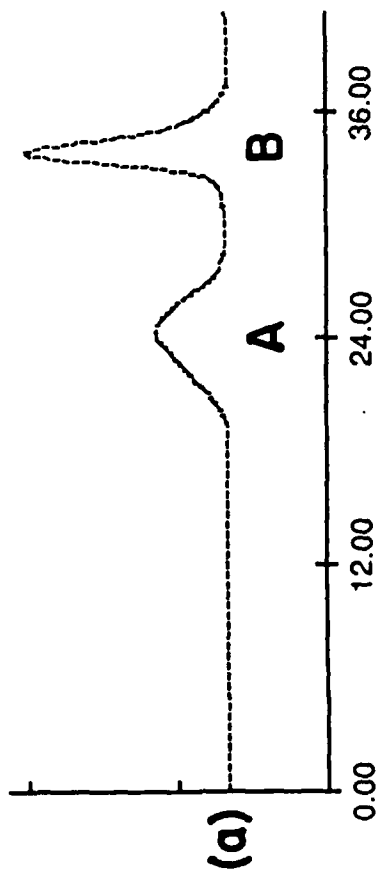
Figure 1



300 MHz ^1H NMR Spectrum of $^t\text{Bu}(\text{CH}=\text{CH})_{11}^t\text{Bu}$
(olefinic protons only)







| peak | M_w | M_n | dispersity |
|------|-----------|---------|------------|
| A | 1,639,000 | 658,300 | 2.49 |
| B | 15,470 | 13,980 | 1.11 |
| C | 153,500 | 151,000 | 1.02 |
| D | 16,790 | 15,200 | 1.11 |

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